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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The crystallization and dielectric properties of strontium titanate aluminosilicate glass-ceramics, containing perovskite $SrTiO_3$ as the primary crystalline phase, have been investigated.

The majority of this research was concentrated on glass-ceramics consisting of 65 wt% of $SrTiO_3$ and 35 wt% of silica and alumina with a silica/alumina weight ratio of 2/1 (SAR-2). In glass-ceramics of this composition, the primary crystalline phase was perovskite $SrTiO_3$; other crystalline phases

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included $SrAl_2Si_2O_8$ (hexacelsiar and anorthite) and TiO_2 (anatase and rutile). The relative amounts of $SrTiO_3$ and the other crystalline phases, and the micro-structure, were a strong function of the crystallization conditions.

The dielectric properties of SAR-2 glass-ceramics were extremely sensitive to the amount of $SrTiO_3$ in the glass-ceramic, and thus to the crystallization conditions. Room temperature dielectric constants of the glass-cearmics ranged from 13 to 47. The dielectric constant increased as the crystallization temperature or time was increased, and peaks developed in the dielectric constant at low temperatures. These dielectric constant peaks were not due to dielectric mixing, and it was proposed that the peaks resulted from ferroic domains in the $SrTiO_3$, possibly caused by an interaction of the $SrTiO_3$ crystallites with the matrix.

Several dielectric loss mechanisms were identified in these glass-ceramics. A temperature-independent (athermal) increase of dielectric loss with frequency (10 kHz to 1 MHz) was observed in all glass and glass-ceramic samples, apparently the result of the low frequency tail of a vibrational loss mechanism. High temperature, low frequency losses were observed in some samples, attributed to Maxwell-Wagner-Sillars effects, caused by the incorporation of Ti^{3+} into the crystalline $SrTiO_3$ phase, and also to the presence of crystal-line titania. Two sets of relaxation-type loss peaks were observed at temperatures near 50 and 100K in certain glass-ceramics; these loss peaks were related to the same mechanism causing the low temperature dielectric constant peaks.

The temperature compensated dielectric response at room temperature originally predicted for the system was confirmed by experiment, however, the escalation of the athermal loss (tan δ) with frequency precludes the use of these glasses in low loss mm wave application.

EVALUATION OF HIGH PERMITTIVITY GLASS CERAMICS FOR
MILLIMETER WAVE APPLICATION

Final Report

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Dr. W.A. Schulze
Dr. L.E. Cross
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S. Swartz
Dr. W. Lawless

May 11, 1985

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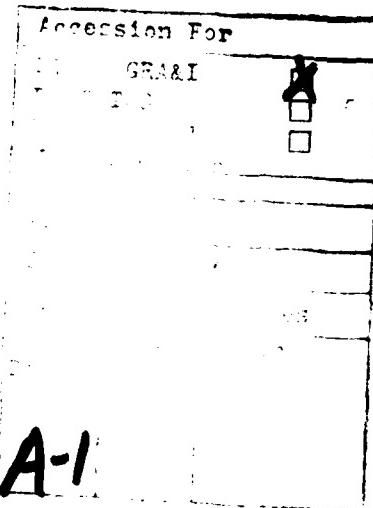
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FOREWORD

This document is the final report on Contract DAAG29-82-K-0015 for the evaluation of high permittivity glass ceramics for millimeter wave applications. The work was initiated by Dr. J. Perison and Dr. W. Schulze in the Department of Electrical Engineering at Penn State. Unfortunately during the contract period, Dr. Perison had to step out from this work due to the death of her husband, and Dr. Walter Schulze took up a new appointment in the Department of Ceramics at Alfred University. Supervision of the ongoing work reverted to Dr. L.E. Cross, Professor of Electrical Engineering, helped by Dr. A.S. Bhalla, Associate Professor of Materials Research, and by Dr. W.N. Lawless of CeramPhysics of Westerville, Ohio, who has acted as a technical consultant for the glass ceramic work.

1.0 STATEMENT OF THE PROBLEM

The initial objective of this work was to make highly transparent low loss glass ceramics in the structure field $SrTiO_3:SiO_2:Al_2O_3$ which could be tailored to have a zero temperature coefficient of permittivity by balancing the strong positive temperature coefficient of the glass against the strong negative temperature coefficient of a perovskite type paraelectric $SrTiO_3$ crystalline phase.

Temperature compensation was explored both theoretically and experimentally and shown to be quite consistent with the properties of the glass and the crystal mixed using the simple Neisel Mixing Rule for composites. Very good low loss properties were achieved in fully oxidized glasses at low frequency, but attempts to use the glass system at high frequency was frustrated by an unexpected athermal loss which escalated rapidly with increasing frequency in all the compositions and for all heat treatments studied.

In an attempt to separate and study the dielectric loss processes in these glass ceramic systems, the phase make up of the crystalline phases occurring during different heat treatments was studied by x-ray diffraction and the dielectric spectra correlated with this phase information.

For the more highly crystalline glasses, quite unexpected peaks were observed in the dielectric permittivity and loss which could not be accounted for by the simple mixing rules. Detailed studies of these phenomena in the temperature range of 4 to 150 K show two dielectric relaxations with activation energies ~0.05 eV and 0.15 eV. Explanations are suggested for both athermal and relaxation type loss processes, but more information is required to prove these hypotheses.

2.0 SUMMARY OF MOST IMPORTANT RESULTS

2.1 Composition

Glasses studied were in the family $SrTiO_3:SiO_2:Al_2O_3$ at the ratio by weight 65% $SrTiO_3$ vs 35% $(SiO_2+Al_2O_3)$. At this ratio two melts were made, SAR-2 with 2:1 ratio silica to alumina and SAR-5 with 5:1 ratio. As a check, batches were made up to Corning Glass Works (C) and at Penn State (P). All melting and "cocktail mixing" to achieve homogeneity was carried out at Corning.

Phases identified on crystallization of these glasses include a precursor phase like $SrTiO_3$ but with larger lattice spacing, $SrTiO_3$ perovskite, $SrAl_2Si_2O_8$ hexacelsion, anorthitic $SrAl_2Si_2O_8$ and rutile TiO_2 with the balance changing markedly with both temperature and time under isothermal recrystallization conditions in the range 800 to 1100°C 1 hour to 64 hours.

Typical sequences with temperature and time are shown in Figures 1 and 2.

2.2 Temperature Compensation

Typical dielectric data for a $SrTiO_3$ glass ceramic SAR-2-P crystallized at 842°C for 1 hour to yield a temperature compensating composition at 20°C is shown in Figure 3. Data were taken at 10,100 and 1,000 kHz on an HP LCR meter under computer control.

Modeled permittivity temperature curves using as input data just the permittivity and temperature coefficients for the pure glass and for $SrTiO_3$ crystals is shown in Figure 4. The general shape is strikingly similar and for the 0.071 volume fraction $SrTiO_3$ required the permittivity of 16.5 is of the same order as the 17.9 measured.

It would appear that the Neisel mixing rule is adequate for these glass ceramics at the low volume fraction loading of $SrTiO_3$ which is required for temperature compensation.

2.3 Athermal Loss

Loss data for an SAR-2-C glass taken over the range -200 to +200°C for both oxidized and unoxidized samples in Figures 5 and 6 typifies the general increasing loss level with increasing frequency which is characteristic of all the samples measured.

The very slow change over a broad temperature range suggests that the loss process is <u>not</u> thermally activated. Slight differences between fully oxidized and unoxidized samples would not indicate in favor of an electronic model. We are tempted to believe that the loss is the broad tail of the vibration losses and may be endemic to all glasses which incorporate heavy cation substituents.

2.4 Low Temperature Relaxations

For more fully crystallized samples (e.g., 16 hours at 1100°C). Two loss processes are evidently operative for both real and imaginary parts of the permittivity, Figures 7 and 8. The obvious dispersion, Figure 9 shows that the processes are thermally activated and activation energies of 0.054 and 0.15 eV have been derived from Arrhenius plots, Figures 10 and 11.

The higher temperature relaxation is accessible to a complete Cole-Cole analysis, Figure 12, showing a broad but symmetrical distribution of relaxation times.

Clearly the lower temperature relaxations are related to the appearance of a well formed $SrTiO_3$ phase. We speculate that the stress boundary conditions in the glass are such that the $SrTiC_3$ may be ferroelectric so that domain wall motion may contribute to the loss process.

4

3.0 PUBLICATIONS, PRESENTATIONS AND REPORTS

3.1 Published Papers

S.L. Swartz, M.T. Lanagan, W.A. Schulze, L.E. Cross and W.N. Lawless, "Dielectric Properties of $SrTiO_3$ Glass-Ceramics," Ferroelectrics 50 (1/2/3/4), 313-318 (1983).

In Preparation

"Characterization of $SrTiO_3$ Glass-Ceramics," to be submitted to J. Amer. Ceram. Soc.

"Low Temperature Dielectric Properties of $SrTiO_3$ Glass-Ceramics," to be submitted to J. Amer. Ceram. Soc.

"Low Temperature Dielectric Properties of $SrTiO_3$ Glass-Ceramics," Proceedings of IMF-6.

3.2 Presentations on $SrTiO_3$ Glass-Ceramics

1. S.L. Swartz, M.T. Lanagan, W.A. Schulze, L.E. Cross and W.N. Lawless, "Dielectric Properties of $SrTiO_3$ Glass Ceramics," presented at the 1983 IEEE International Symposium on Applications of Ferroelectrics, Gaithersburg, MD, June 1983.

2. S.L. Swartz, M.T. Lanagan, B.H. Fox and L.E. Cross, "Dielectric Properties of $SrTiO_3$ Glass-Ceramics," presented at the 1984 Annual Spring Meeting of the American Ceramic Society, Pittsburgh, PA, April 1984.

3. S.L. Swartz, B.H. Fox and E. Breval, "A Structural Study of $SrTiO_3$ Glass-Ceramics," presented at the 1984 Fall Glass Division Meeting of the American Ceramic Society, Grossingers, NY, October 1984.

4. S.L. Swartz, A.S. Bhalla and L.E. Cross, "Low Temperature Dielectric Properties of $SrTiO_3$ Glass-Ceramics," presented at the 1984 Fall Electronics Division Meeting of the American Ceramic Society, San Francisco, CA, October 1984.

Forthcoming

"Low Temperature Dielectric Properties of $SrTiO_3$ Glass-Ceramics," to be presented at IMF-6, Kobe, Japan, August 1985.

3.3 Presentations at National and International Meetings

4.0 THESIS

Much of the work carried out on this program is discussed in detail in the Ph.D. thesis of Scott Swartz who was supported on contract funds. His thesis entitled, "Dielectric Properties of Strontium Titanate Glass Ceramics," is included in Appendix 3.

5.0 PARTICIPATING SCIENTIFIC PERSONNEL

Work on the contract was initiated by Dr. J. Perison and Dr. W. Schulze, however, as discussed in the Foreword, these investigators left the University and the supervision was carried out by Dr. L.E. Cross and Dr. A.S. Bhalla. Over the full period of the contract, Dr. W.N. Lawless has provided consulting service in the special area of $SrTiO_3$ glasses.

The majority of experimental work was carried out by Scott Swartz, a graduate student in Solid State Science and is used in his thesis dissertation which is included as Appendix 3. Additional support was provided by Paul Moses who supervises dielectric measurements and is in charge of all software development for the automatic measuring systems.
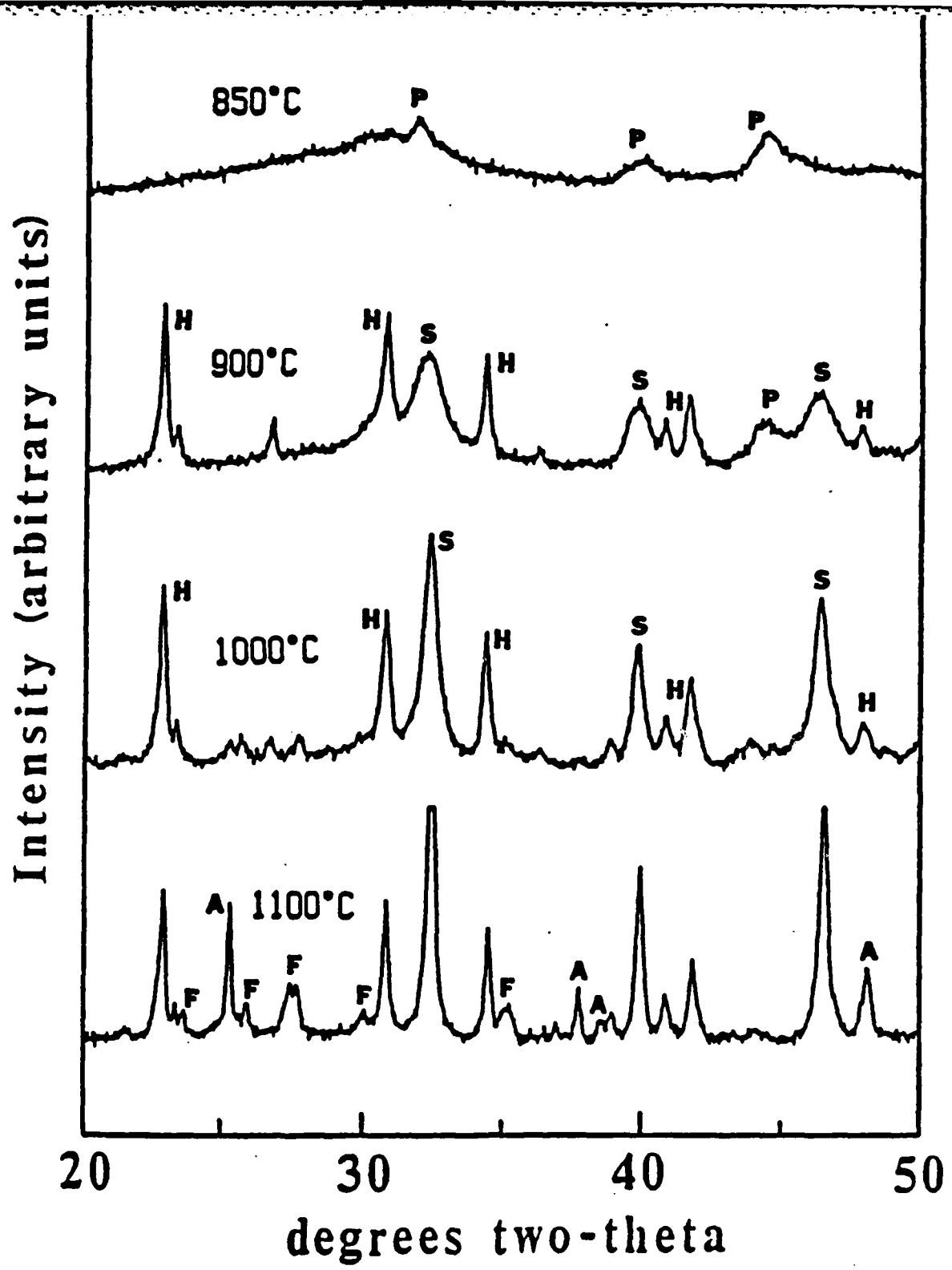
Figure 1. XRD patterns of SAR-2-P glass-ceramics, crystallized at various temperatures for one hour. Phases indicated as: P) precursor phase and S) perovskite $SrTiO_3$; H) hexacelsian and anorthite $SrAl_2Si_2O_8$; A) anatase TiO_2.
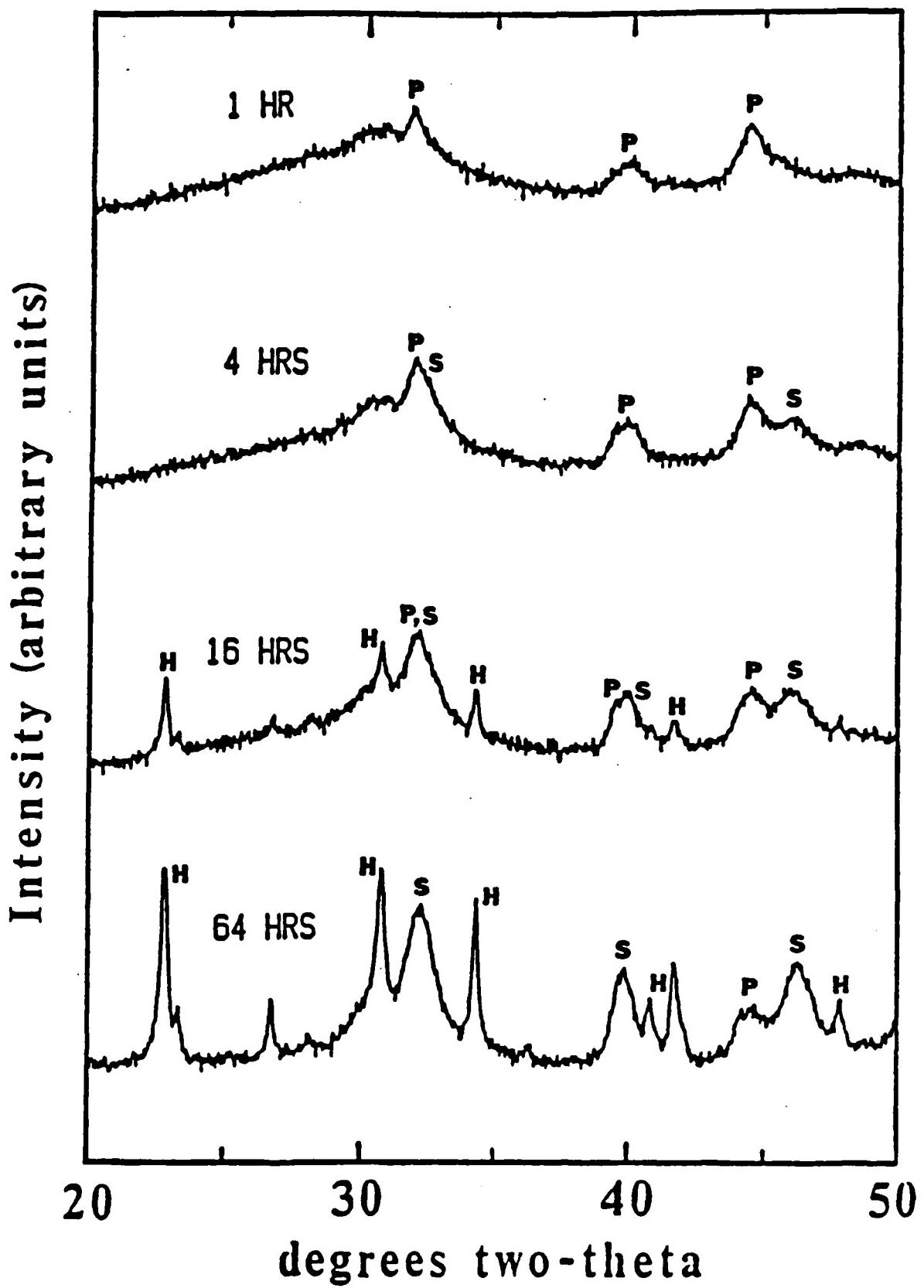
Figure 2. XRD patterns of SAR-2-P glass-ceramics, crystallized at 850°C for various times. Phases indicated as: P) precursor phase and S) perovskite $SrTiO_3$; H) hexacelsian $SrAl_2Si_2O_8$.
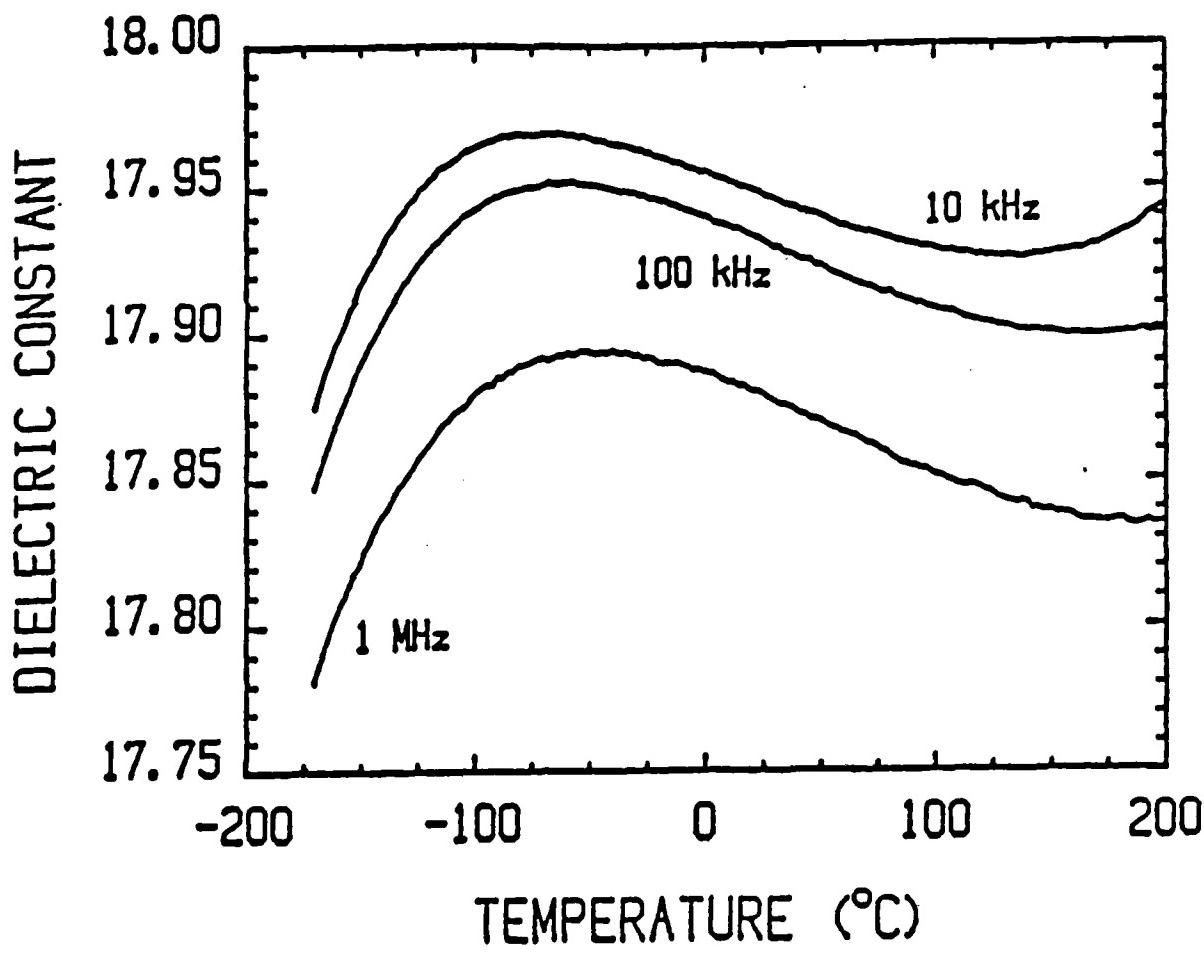
Figure 3.   Dielectric constant at 10, 100, and 1000 kHz
versus temperature, for the SAR-2-P glass-
ceramic, conventionally crystallized at 842°C
for one hour.
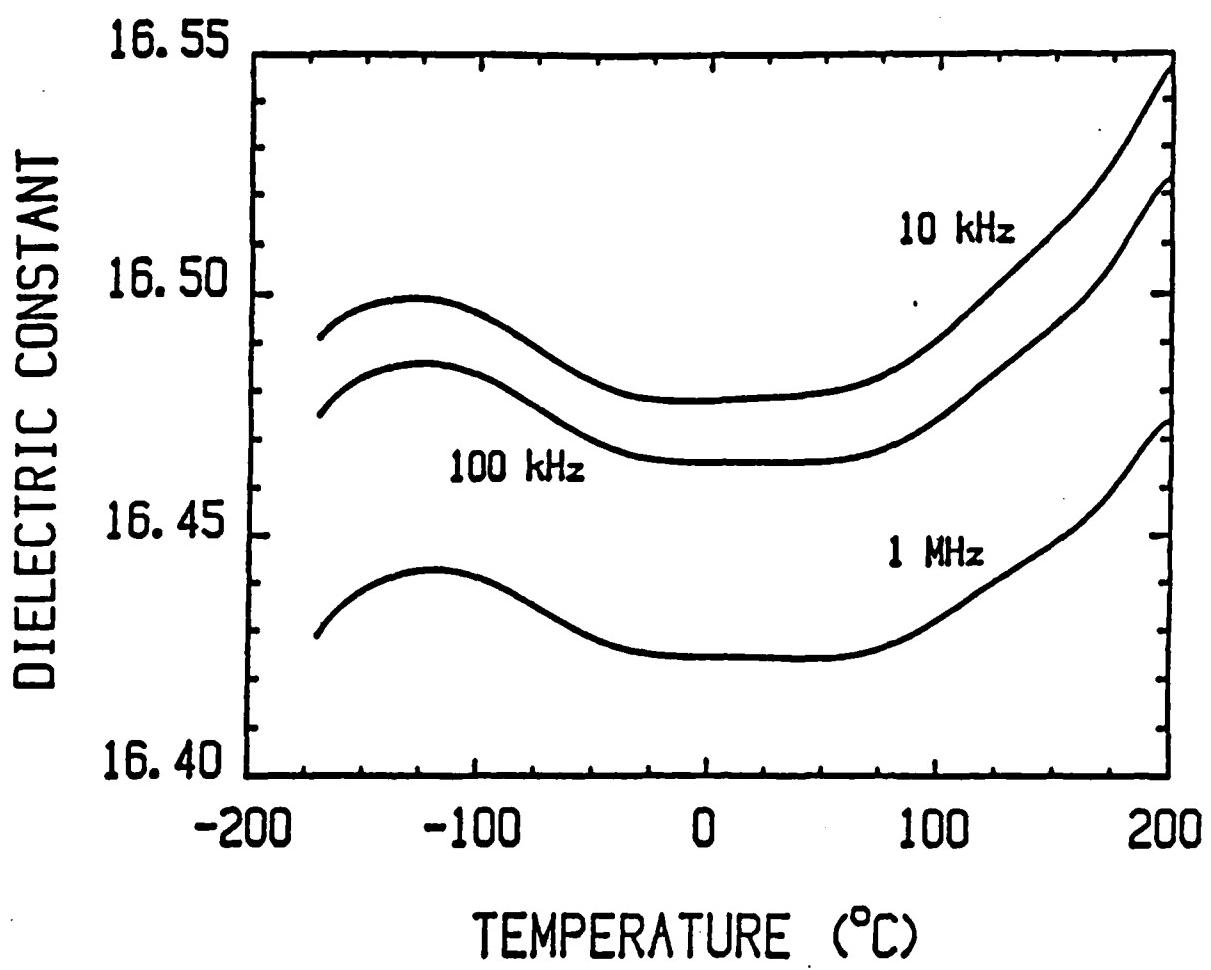
Figure 4.   Modelled dielectric constant at 10, 100, and
1000 kHz versus temperature, for glass-ceramic
with TCC equal to zero (volume fraction of
$SrTiO_3$ equals 0.071).
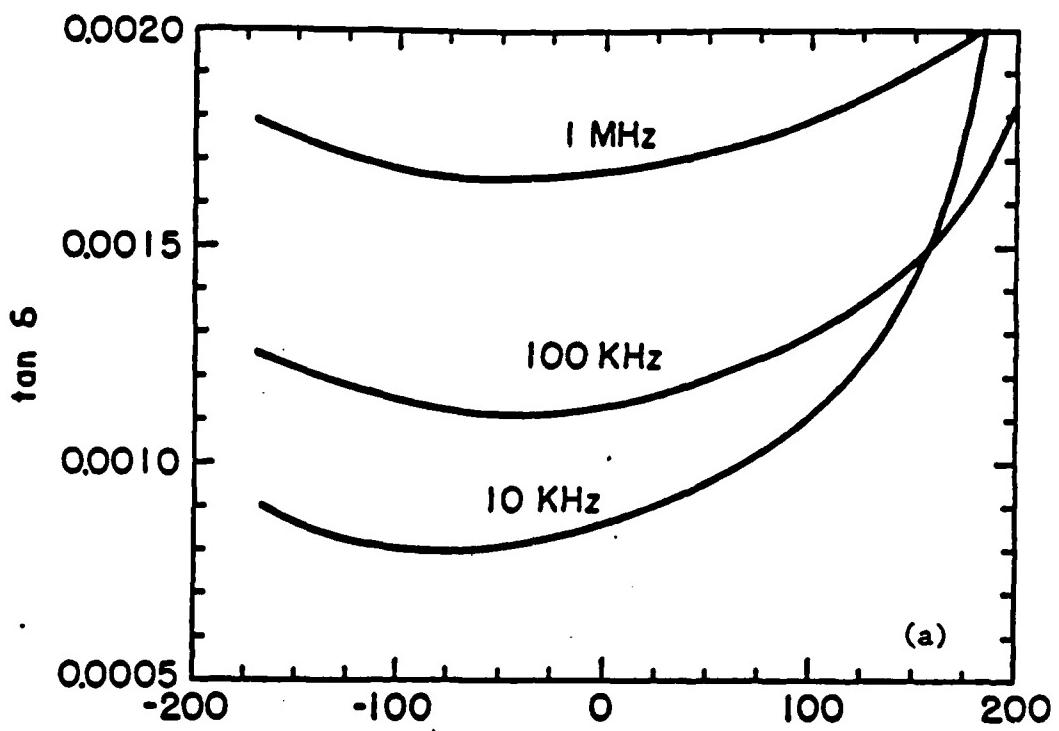
Figure 5. Dissipation factor at 10, 100, and 1000 kHz versus temperature, for unoxidized SAR-2-C glass.
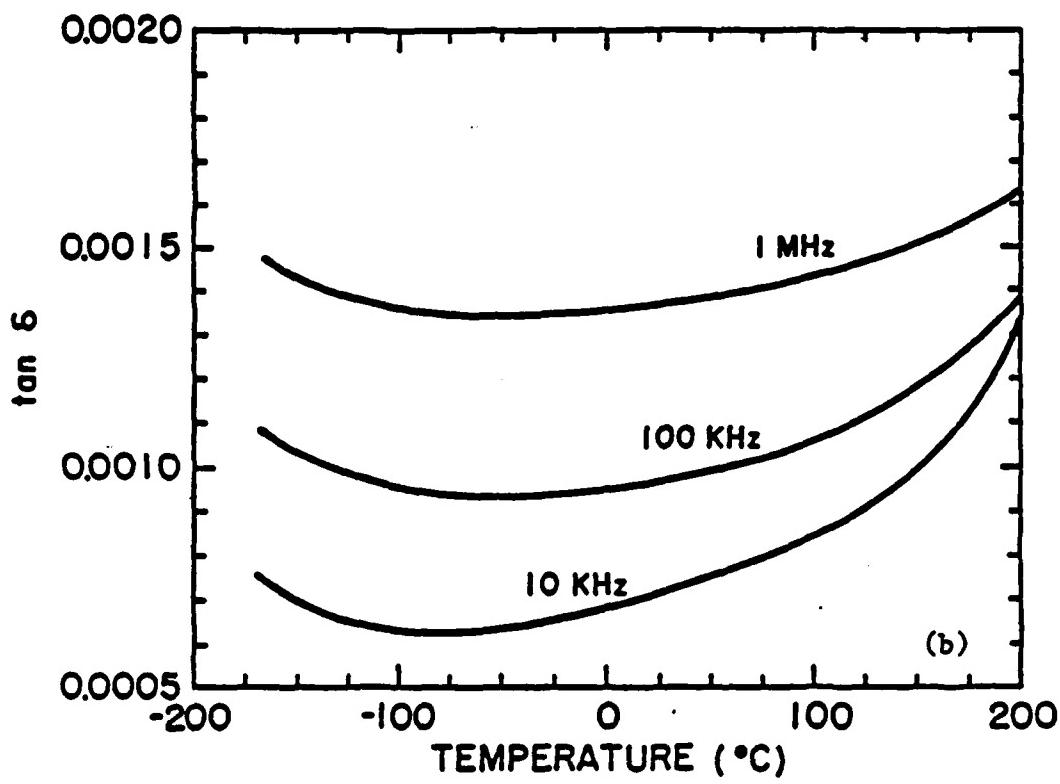
Figure 6. Dissipation factor at 10, 100, and 1000 kHz versus temperature for oxidized SAR-2-C glass.
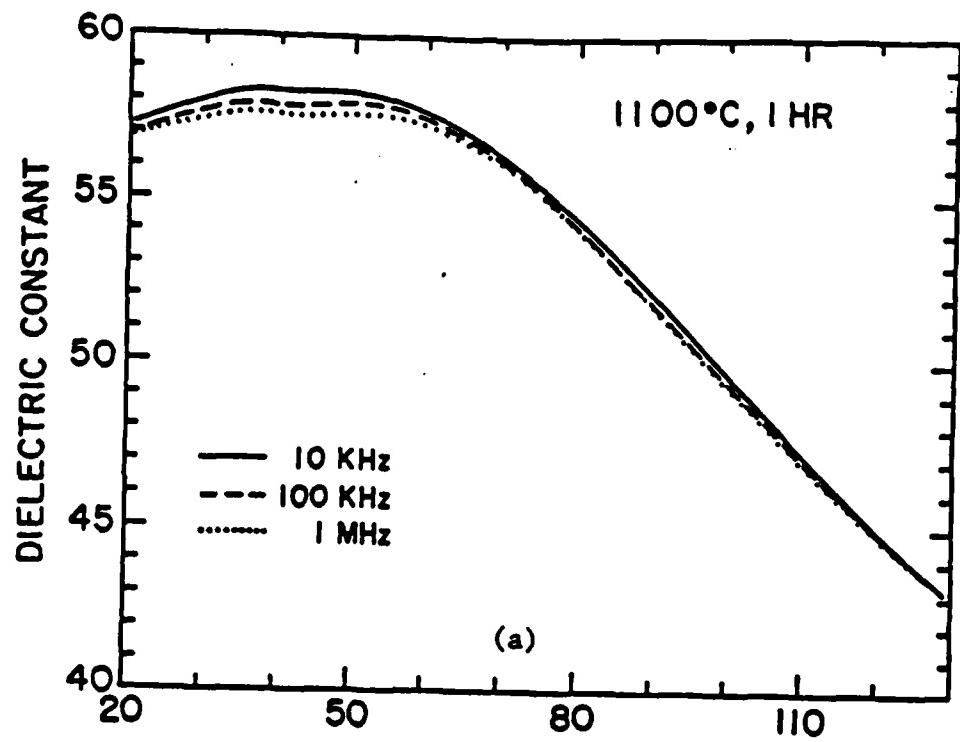
Figure 7. Dielectric constant at 10, 100, and 1000 kHz versus
temperature, for the SAR-2-P glass-ceramic, isothermally
crystallized at 1100°C for one hour, over the temperature
ranges 20 to 130K.
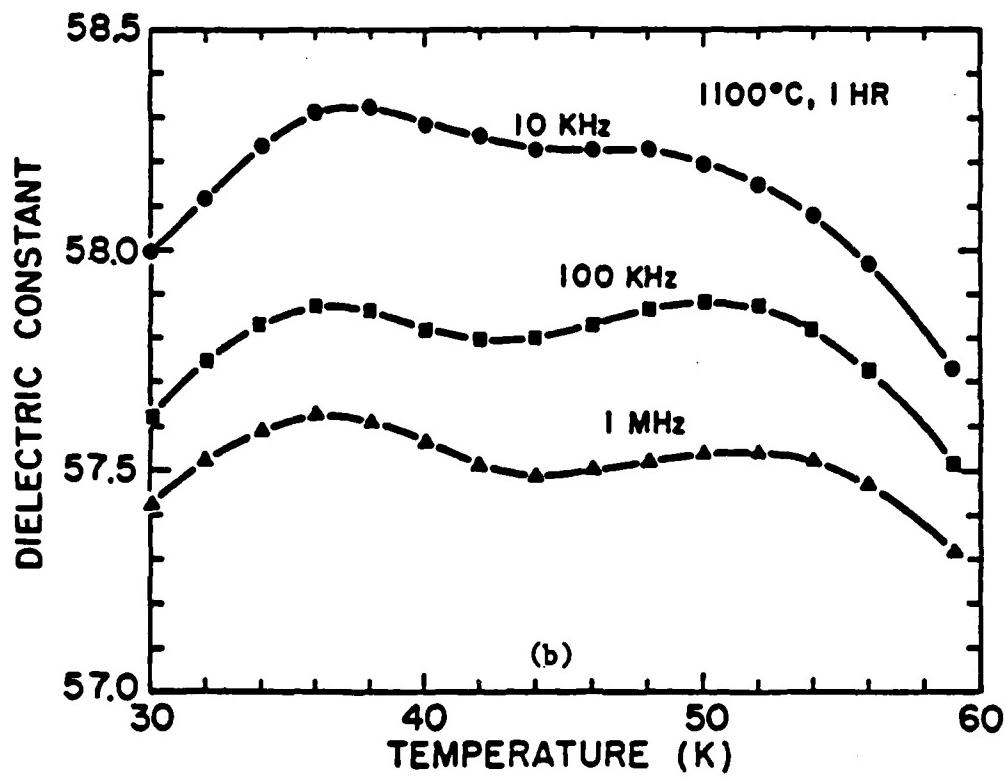
Figure 8. Dielectric constant at 10, 100, and 1000 kHz versus temperature, for the SAR-2-P glass-ceramic, isothermally crystallized at 1100°C for one hour, over the temperature ranges 30 to 60K.
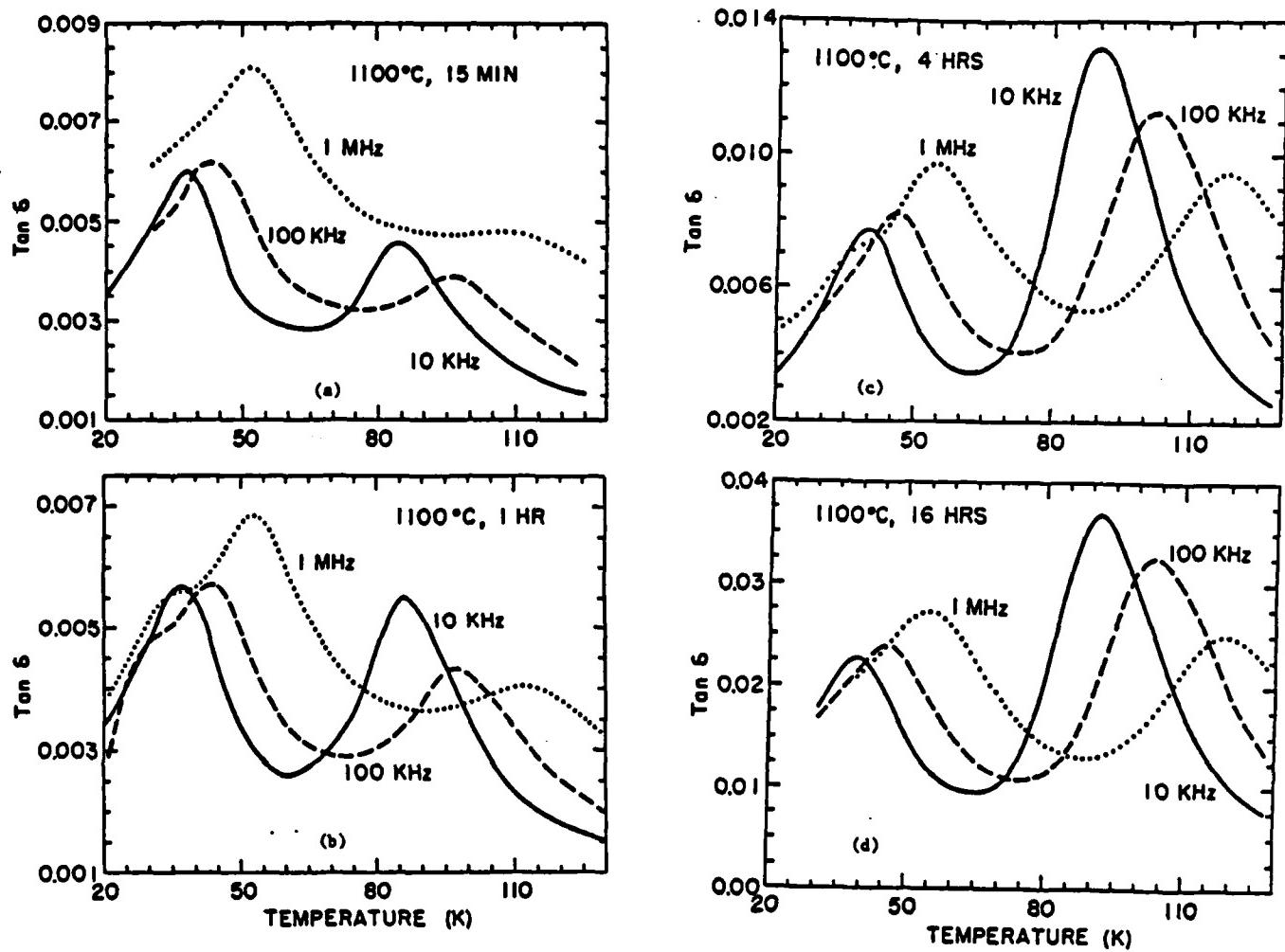
Figure 9.   Dissipation factor at 10, 100, and 1000 kHz
             versus temperature, for SAR-2-P glass-
             ceramics, isothermally crystallized at 1100°C
             for: a) 15 minutes, b) one hour, c) four
   hours, and d) 16 hours.
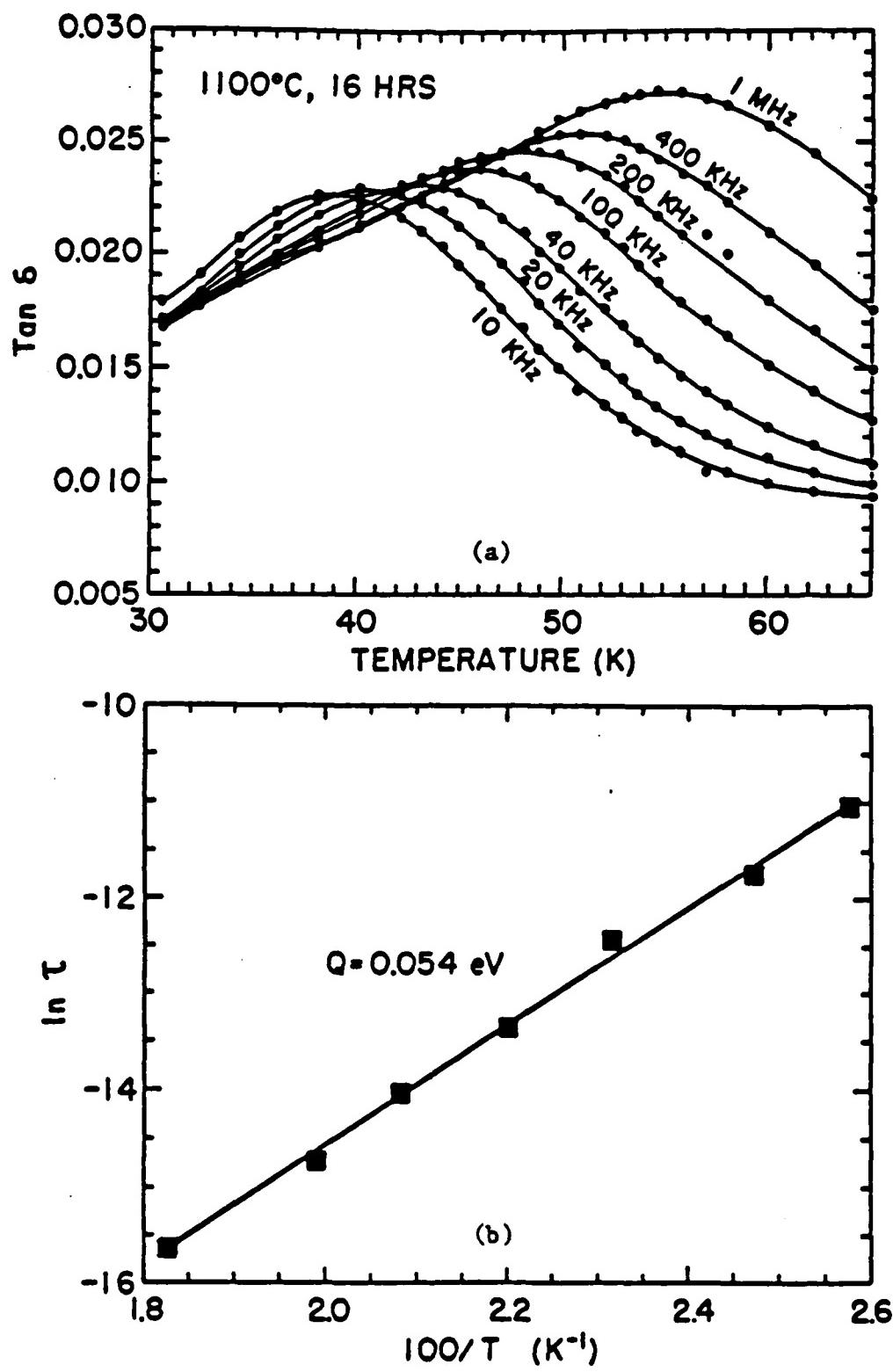
Figure 10.   a) Dissipation factor at seven frequencies
between 10 and 1000 kHz versus temperature
(30 to 65K), and b) corresponding Arrhenius
plot, for the SAR-2-P glass-ceramic,
isothermally crystallized for 16 hours.
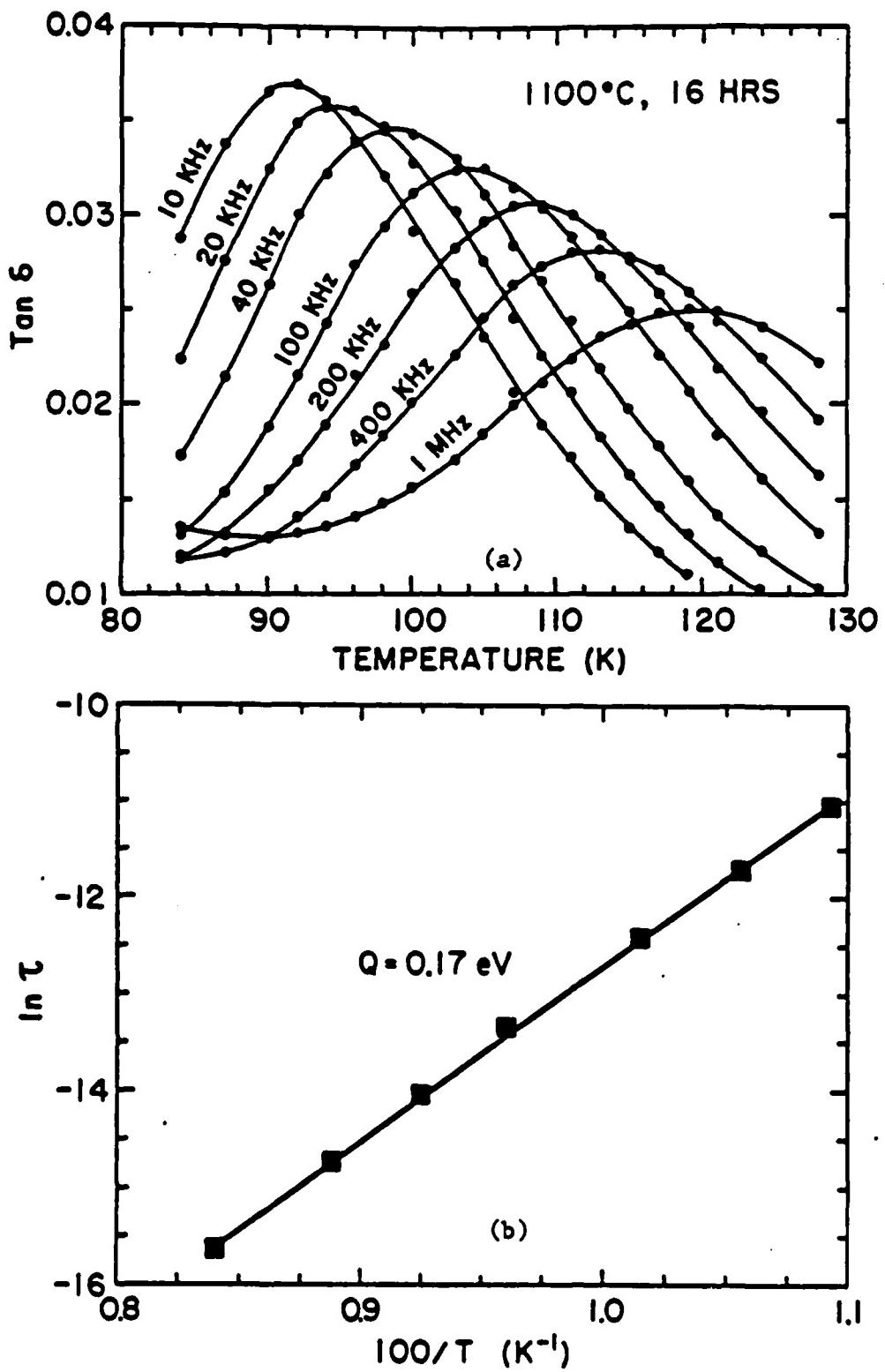
Figure 11. a) Dissipation factor at seven frequencies
between 10 and 1000 kHz versus temperature
(80 to 130K), and b) corresponding Arrhenius
plot, for the SAR-2-P glass-ceramic,
isothermally crystallized for 16 hours.
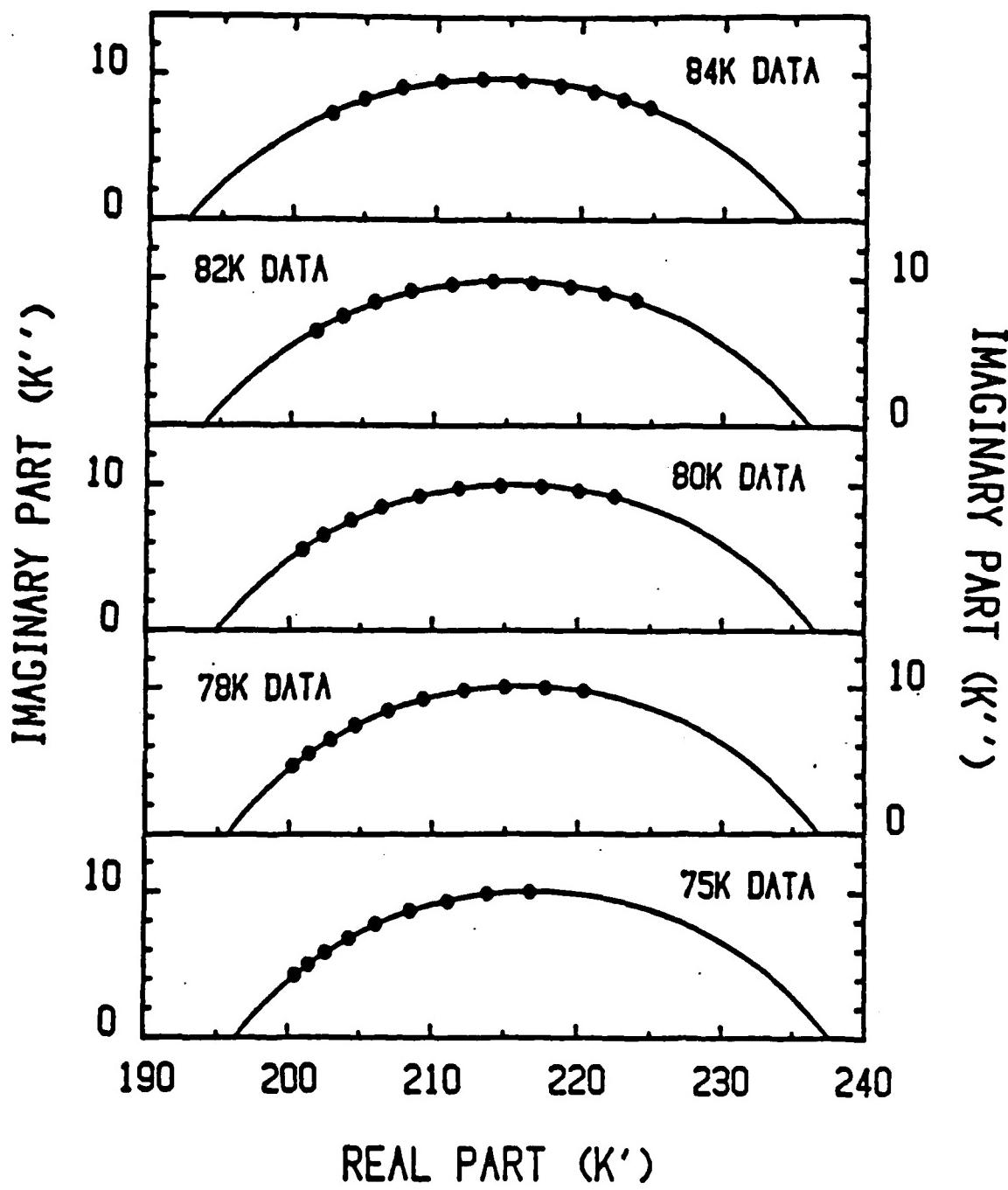
Figure 12.   Comparison of Cole-Cole arcs, constructed from
dielectric data taken at 75, 78, 80, 82, and
84K, for the SAR-2-P glass-ceramic, isothermally
crystallized at 1100°C for 16 hours.

APPENDIX 1

DIELECTRIC PROPERTIES OF $SrTiO_3$ GLASS-CERAMICS

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Abstract Strontium titanate glass-ceramics, prepared by the crystallization of strontium titanate-aluminosilicate glasses have been investigated for possible application as low-loss dielectric materials at microwave and millimeter wave frequencies. Under suitable crystallization conditions, these glass-ceramics exhibit temperature compensated dielectric permittivity, a consequence of the balance between the negative temperature coefficient of the $SrTiO_3$ crystalline phase and the positive temperature coefficient of the residual aluminosilicate glass phase. Temperature coefficients of less than 10 ppm/°C with dielectric constants in the range of 16-18 have been achieved over a temperature range of -55 to 125°C. Dielectric losses at frequencies up to 4MHz are extremely low (tan δ < 0.0005). However, dielectric measurements in the range of 100-1000MHz have shown that the losses increase as the frequency approaches the millimeter wave region, indicating that these glass-ceramics might not be acceptable as millimeter wave dielectrics.

INTRODUCTION

Glass-ceramics are polycrystalline solids, products of the controlled crystallization of glasses.[1] The microstructure of a typical glass-ceramic can be described as a homogeneous, porosity-free matrix of very fine crystallites, interwoven with a residual glass phase. This type of microstructure is ideally suited for the study and optimization of dielectric properties, especially the aspects of zero porosity and a fine and uniform crystallite size. Accordingly, there have been several investigations into the dielectric properties of certain glass-ceramic systems in which the major crystalline phase is a ferroelectric compound, such as the $BaTiO_3$[2], $PbTiO_3$[3], and $NaNbO_3$[4]. The potential applications for this family of glass-ceramic dielectrics are numerous and have been reviewed by Herczog.[5]

In this investigation, the dielectric properties of glass-ceramics in the $SrTiO_3-SiO_2-Al_2O_3$ system have been studied. Applica-

tions of $SrTiO_3$ glass-ceramics have heretofore been limited to cryogentic temperatures and include a capacitance thermometer, a dielectric bolometer, and a capacitive energy storage dielectric.[6] This glass-ceramic system was selected for study at higher temperatures because a preliminary investigation demonstrated that the temperature coefficient of dielectric permittivity in these glass-ceramics in positive prior to and during the intial stages of crystallization; as more $SrTiO_3$ is precipitated from the glass, the temperature coefficient decreases, and eventually becomes negative.[7] Thus, a potential exists for temperature compensated dielectric permittivity if suitable crystallization conditions are employed.

The purpose of this investigation is two-fold: to better characterize the above mentioned crossover of the temperature coefficient of dielectric permittivity and to make dielectric measurements over a wide frequency range in an effort to gain an understanding of dielectric loss mechanisms in these glass-ceramics. The long range goal of this research effort is to develop better materials for high frequency applications.

GLASS COMPOSITIONS, MELTING, AND CRYSTALLIZATIONS

Two glass compositions were investigated, each with 65% by weight of $SrTiO_3$ and the remaining 35% being comprised of SiO_2 and Al_2O_3, with silica/alumina weight ratios (SAR's) of 2 and 5. The glasses were batched and melted at the Corning Glass Works in Corning, New York. The melting procedure consisted of melting the glasses in platinum crucibles at 1625°C for two hours with "cocktail mixing" to assure homogeneity. The molten glasses were poured into copper molds so that one inch thick slabs, four by six inches, were formed. The glass slabs were then annealed at 760°C overnight.

Differential thermal analysis (DTA) was used to monitor any glass transformations or crystallizations occurring in the two glasses. DTA patterns were run from room temperature to 1200°C with a heating rate of 10°C/minute. Each of the glasses exhibited an endothermic peak corresponding to a glass transition temperature of 760°C, and a large exothermic peak at 900°C, presumably corresponding to the crystallization of $SrTiO_3$. Secondary crystallizations occurred at 1000 and 1090°C for the glass with SAR = 2 and 1160°C for the glass with SAR = 5.

Disc shaped samples, 9mm in diameter and one millimeter in thickness, were cut from the glass slabs to be used for crystallization studies and dielectric measurements. Crystallizations were carried out on the small glass discs by heating in a microprocessor controlled electric resistance furnace at a rate of 100°C/hour to a crystallization temperature (maintained ± 1°C) in the range of 800-900°C for a soak time of one or ten hours, followed by cooling at 100°C/hour.

X-ray diffraction analysis was carried out utilizing on an automated x-ray diffraction system, with scans being run from 20-50°2θ (CuKα radiation) with 0.03° increments and count times of one second. X-ray diffraction patterns of glass-ceramics of both compo-

sitions, crystallized at various temperatures, appear in Figure 1. The most surprising result in the x-ray analysis is that, for both glass compositions, as the crystallization temperature is increased, the first phase to appear in the x-ray patterns is not $SrTiO_3$, but an unidentified alumino-silicate phase. As the crystallization temperature is further increased, peaks corresponding to $SrTiO_3$ become evident. This observation is not particularly disturbing, however. In the initial stages of crystallization, the $SrTiO_3$ crystallite size could very well be too small for x-ray diffraction to be able to detect any $SrTiO_3$. Another observation from the x-ray data is that the aulumino-silicate phase is more abundant in the glass with SAR = 5 than for SAR = 2.
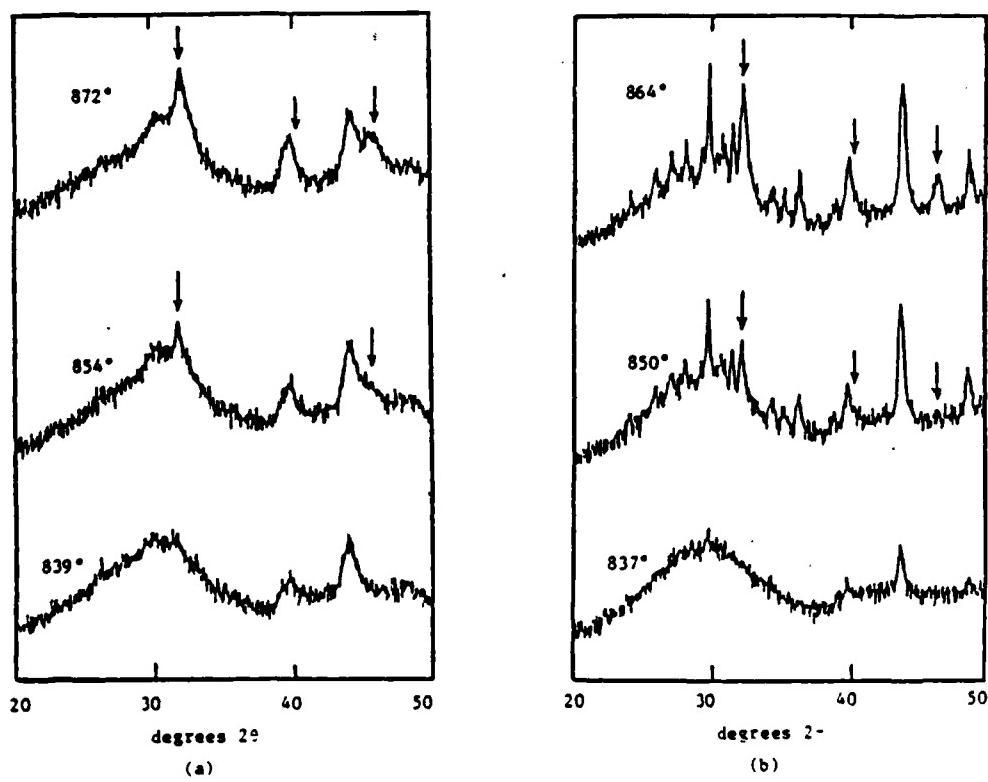

FIGURE 1   X-ray diffraction scans of the two glass composi-
           sitions, crystallized at various temperatures for
           one hour for a) SAR = 2 and b) SAR = 5 (arrows
           indicates $SrTiO_3$ peaks).

DIELECTRIC MEASUREMENTS

Samples for dielectric measurements were prepared by polishing the glass-ceramic discs parallel with 25μm alumina, sputtering gold electrodes, and applying air-dry silver paints to improve electrical contact. Low frequency, weak field dielectric measurements were carried out as a function of temperature utilizing a computer automated system. Dielectric permittivity (capacitance) and dissipation

factor at several frequencies between 10KHz and 4MHz were measured pseudo-continuously on cooling from 150 to -160°C at a rate of 3°C/ minute. Temperature coefficients of dielectric permittivity (or more accurately, temperature coefficients of capacitance, since a correction for thermal expansion was not applied) were calculated by fitting the dielectric constant (at 1MHz) vs. temperature data between -55 and 125°C to a straight line and dividing the slope by the value of the dielectric constant at 25°C.

Dielectric data are presented in Figures 2a and 2b, which are respectively, the room temperature dielectric constants (at 1MHz) and temperature coefficients plotted as a function of crystallization temperature for both glass compositions (SAR = 2 and SAR = 5) and crystallization times (one and ten hours). Analysis of these dielectric data led to the following observations.

1. The dielectric constant and the temperature coefficient decreased as the crystallization temperature was increased, even at temperatures below which $SrTiO_3$ was detected by x-ray diffraction.

2. The crossover of the sign of the temperature coefficient occurred at 840 and 860°C for one hour crystallizations of the glass compositions corresponding to silica/alumina weight ratios of 2 and 5, respectively.

3. For both glass compositions, ten hour crystallizations effectively decreased the crossover crystallization temperature by about 30°C.

4. The magnitudes of the dielectric constant at the crossover were 17.5 and 16.0 for glass compositions SAR = 2 and SAR = 5, respectively.

5. The low frequency (10KHz - 4MHz) dissipation factors of these glass-ceramics, over the range of compositions and crystallization temperatures investigated, were generally too low to be measured accurately (tan δ < 0.0005).
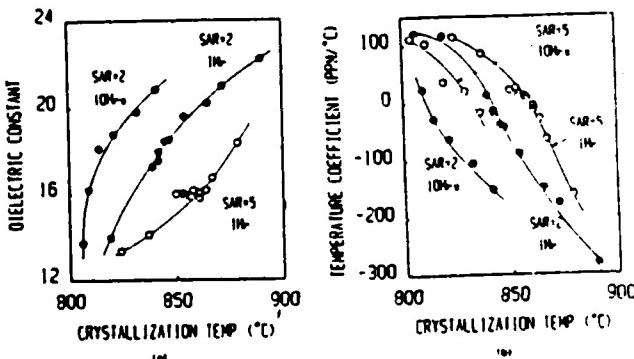

FIGURE 2 a) Dielectric constant and b) temperature coefficient vs. crystallization temperature for various glass compositions and crystallization conditions.

The temperature dependences of the dielectric constant of SAR = 5 glass-ceramics, crystallized near the crossover, are shown in Figure 3a, in which plots of capacitance (at 1MHz), normalized to 0°C, vs. temperature are presented for a series of glass-ceramic discs, crystallized at 857, 858, and 861°C. The frequency dependence of an SAR = 5 glass-ceramic, crystallized at 861°C for one hour, is demonstrated by Figure 3b, which gives plots of normalized capacitance vs. temperature at frequencies of 10KHz, 100KHz, and 1MHz. The temperature dependences of SAR = 2 glass-ceramics, crystallized near the crossover, are similar to those of SAR = 5 glass-ceramics, shown in Figure 3.
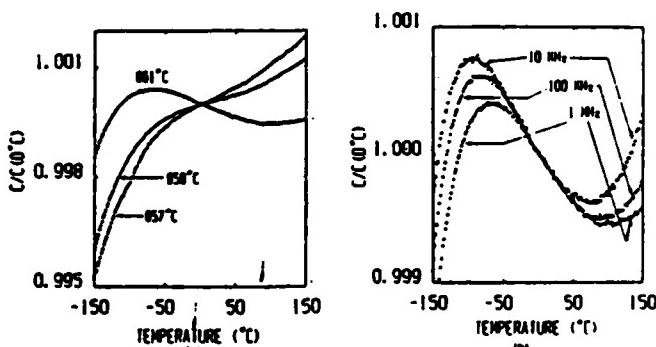

FIGURE 3   Normalized capacitance vs. temperature for: a) SAR=5 glass-ceramics, crystallized at various temperatures for one hour; and b) SAR=5 glass-ceramic, crystallized at 861°C for one hour at various frequencies.

The most obvious features of the dielectric constant vs. temperature curves of these glass-ceramics, crystallized near the crossover, are a maximum in the dielectric constant at low temperature ($\sim$−100°C) and a minimum at some higher temperature ($\sim$100°C). This can be understood solely on the basis of the dielectric mixing of the two phases in the glass-ceramic. At low and high temperatures, the positive temperature coefficient of the glass phase dominates the dielectric response, while at intermediate temperatures, the negative temperature coefficient of the $SrTiO_3$ phase dominates.

Dielectric measurements of selected glass and glass-ceramic samples in the 100MHz - 1GHz range were made at room temperature on a resonant coaxial line system. Capacitance (dielectric constant) and quality factor (1/tan δ) were calulated at frequencies (depending on sample geometry) of about 190, 420, 670, and 920 MHz. The dielectric losses in this frequency range were an order of magnitude larger than at lower frequencies ($\sim$1MHz), and increased significantly as the frequency was increased. The origin of the increased losses is unknown, but it is likely that the losses will remain high or continue to increase as the frequency is raised into the millimeter wave region.

SUMMARY

The results of this investigation are summarized below:

1. $SrTiO_3$ can be crystallized from glasses in the $SrTiO_3$-SiO_2-Al_2O_3 system by heat treatments in the range of 800-900°C.

2. The temperature coefficient of dielectric permittivity in these glasses is positive prior to crystallization, and then decreases and becomes negative as the crystallization temperature is increased (i.e., as more $SrTiO_3$ is precipitated from the glass).

3. $SrTiO_3$ glass-ceramics were prepared with dielectric constants in the range of 16-18 and temperature coefficients of less than 10ppm/°C.

4. Dielectric losses in these glass-ceramics are quite low (tan δ < 0.0005) at frequencies below 10MHz, but increase significantly over the frequency range of 100MHz to 1GHz as the frequency approaches the millimeter wave region.

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APPENDIX 2

LOW TEMPERATURE DIELECTRIC PROPERTIES OF $SrTiO_3$ GLASS-CERAMICS

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ABSTRACT

The low temperature dielectric properties of a particular $SrTiO_3$-containing glass-ceramic have been investigated. This glass-ceramic exhibited a dispersive dielectric constant peak over the temperature range of 85 to 100K and relaxation-type loss peaks at temperatures near 50 and 100K. Arrhenius plots of dielectric loss data gave activation energies of 0.054 and 0.17 eV for the lower (50K) and higher (100K) temperature loss mechanisms. The higher temperature loss mechanism was further analyzed by the Cole-Cole method, and a relaxation strength (K_s-K_∞) of 41 was calculated. The dielectric constant peak was related to the higher temperature loss mechanism, and it was proposed that ferroic phenomena were responsible.

INTRODUCTION

Strontium titanate glass-ceramics have been utilized for several years as cryogenic capacitive temperatures sensors[1]. Their usefulness is based on a peak in the dielectric constant at a temperature near 77K. However, the nature of this dielectric constant peak has not been clearly defined. Lawless[2] attributed

1

the dielectric constant peaks to an anti-ferroelectric transition in the $SrTiO_3$ phase, while Siegwarth[3] suggested that they were caused by the relaxation of electret (defect-dipole) states in the $SrTiO_3$, although definitive dielectric loss data supporting these proposed mechanisms were not presented. In this paper, low temperature dielectric constant and loss measurements of a similar $SrTiO_3$ glass-ceramic will be reported.

GLASS-CERAMIC PREPARATION AND CHARACTERIZATION

Glass-ceramics were derived from a glass with a nominal composition consisting of 65 wt% $SrTiO_3$, 23 wt% SiO_2, and 12 wt% Al_2O_3, prepared by melting at 1650°C for two hours and annealing at 760°C. The crystallization and dielectric properties of these glass-ceramics have recently been investigated[4]. The dielectric measurements to be described in this paper were performed on glass-ceramic disks crystallized isothermally for 16 hours at 1100°C. Generally, in this glass-ceramic, perovskite $SrTiO_3$ was the primary crystalline phase. Secondary crystalline phases were anorthite $SrAl_2Si_2O_8$ and anatase TiO_2. The microstructure of this glass-ceramic consisted of sub-micron dispersed $SrTiO_3$ crystallites and large acicular anatase crystals of up to 80 microns in length. The matrix consisted of anorthite $SrAl_2Si_2O_8$ and a residual glass containing silica and alumina.

DIELECTRIC MEASUREMENTS

The dielectric constant versus temperature at several frequencies between 10 and 1000 kHz appears in Figure 1. The dielectric constant peak was extremely frequency-dependent. The magnitude of the dielectric constant peak varied from 204 at 10

2

kHz to 191 at 1 MHz, and the peak occurred near 100K for frequencies between 10 and 100 kHz, and at 85K for a frequency of 1 MHz. The dispersive nature of the dielectric constant peaks suggested dielectric loss phenomena.

The low temperature dielectric loss behavior of this sample was dominated by two sets of relaxation-type dielectric loss peaks at temperatures near 50 and 100K. Dielectric loss spectra (dissipation factor versus temperature at seven frequencies between 10 and 100 kHz) in the temperature ranges of the two loss mechanisms appear, along with the corresponding Arrhenius plots, in Figures 2 and 3. For both of the dielectric loss mechanisms, the loss peak temperature increased with frequency, from about 38 to 52K and 85 to 100K, over the frequency range of 10 to 1000 kHz. The activation energies, calculated from the Arrhenius plots, were 0.054 and 0.17 eV for the lower (50K) and higher (100K) temperature loss mechanisms, respectively. The magnitude of the higher temperature loss peak decreased and the peak broadened with increasing frequency, while the magnitude of the lower temperature loss peak increased and the peak sharpened with increasing frequency.

Very precise dielectric measurements were made over the frequency range of 0.1 to 10 kHz to various temperatures, chosen so that the higher temperature dielectric loss mechanism could be studied. Dielectric data are presented as plots of dissipation factor versus log frequency at a series of temperatures between 73 and 84K in Figure 4. Dielectric loss peaks with frequency were observed at each of these temperatures, and the frequency of

the loss peak increased with temperature, as expected for a relaxation-type loss mechanism.

The low frequency dielectric data was further analyzed by the Cole-Cole method. A Cole-Cole plot, constructed from dielectric data taken at 82K, is presented in Figure 5; the line between the K_∞ intercept and the origin of the arc is shown, defining the tilt angle. The effect of temperature on the relaxation process was determined by performing the Cole-Cole analysis on the dielectric data taken at temperatures of 75, 78, 80, 82, and 84K. The data indicated a relaxation strength ($K_s - K_\infty$) of about 41, and that K_∞ (the value of the dielectric constant without the contribution of the loss mechanism) decreased from 196.3 to 192.6 as the temperature was increased from 75 to 84K. The latter observation was in contradiction with the original data, in which the dielectric constant increased with temperature at constant frequency in this range. This can be explained by the shift in the relative positions of the data points along the Cole-Cole arc with increasing temperature, as shown in Figure 6 for a series of Cole-Cole arcs for five temperatures between 75 and 84K. At 75K, the dispersion corresponding to this loss mechanism occurred on the high frequency portion of the arc. As the temperature was increased, the dispersion shifted to lower frequencies, thus increasing the contribution of the loss mechanism to the dielectric constant. From these data it can be concluded that the anomalous shape of the dielectric constant peak was related to the higher temperature loss mechanism.

DISCUSSION

From the above data, and in data not presented in this paper, it was clear that the dielectric constant peaks were the result of an interaction of the $SrTiO_3$ phase with the matrix. The defect-dipole mechanism proposed by Siegwarth[3] is immediately ruled out for two reasons: 1) the dielectric constant peaks would not have been as sensitive to the nature of the matrix; and 2) the decrease of the dielectric constant with an applied electric field of 20 kV/cm was much larger than the relaxation strength (K_s-K_∞). Some sort of ferroic phenomenon was suggested by the data. The higher temperature loss mechanism was consistent with ferroic domain effects, and the temperature of this loss mechanism was close to the known ferroelastic transition at 100K in $SrTiO_3$. The complicated stresses exerted by the matrix on the $SrTiO_3$ as the glass-ceramic was cooled below the 110K transition of $SrTiO_3$ could have resulted in a number of possible ferroic interactions. The exact natures of these phenomena are still under investigation.

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FIGURE CAPTIONS

Figure 1. Dielectric constant versus temperature for various measurement frequencies.

Figure 2. Dielectric loss spectra and corresponding Arrhenius plot for the lower temperature loss mechanism.

Figure 3. Dielectric loss spectra and corresponding Arrhenius plot for the higher temperature loss mechanism.

Figure 4. Dissipation factor versus log frequency at various temperatures.

Figure 5. Cole-Cole plot constructed from dielectric data taken at 82K, corresponding to the higher temperature loss mechanism.

Figure 6. Comparison of Cole-Cole arcs, constructed from dielectric data taken at various temperatures between 75 and 84K.
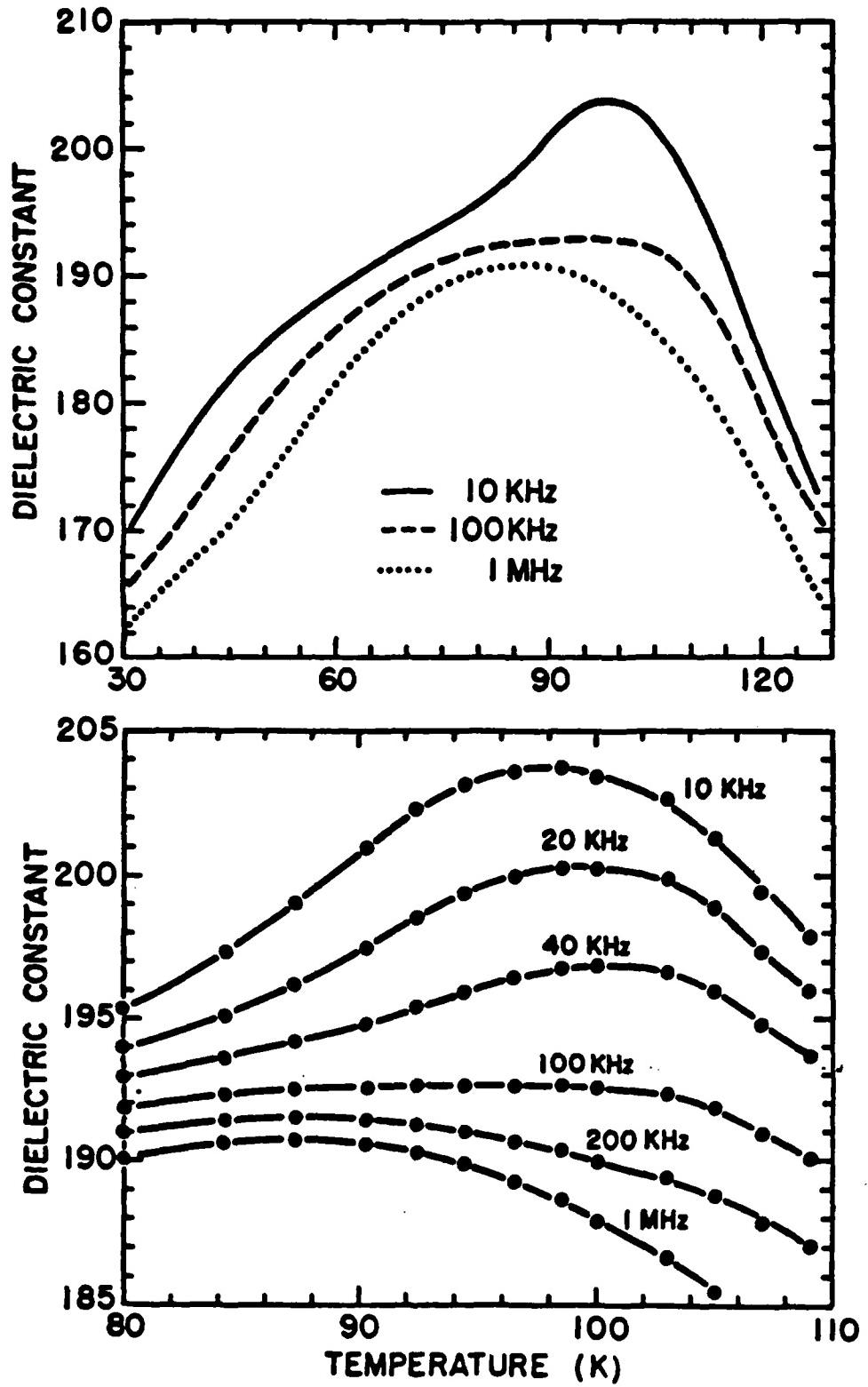
Figure 1
8.5 × 15 mm
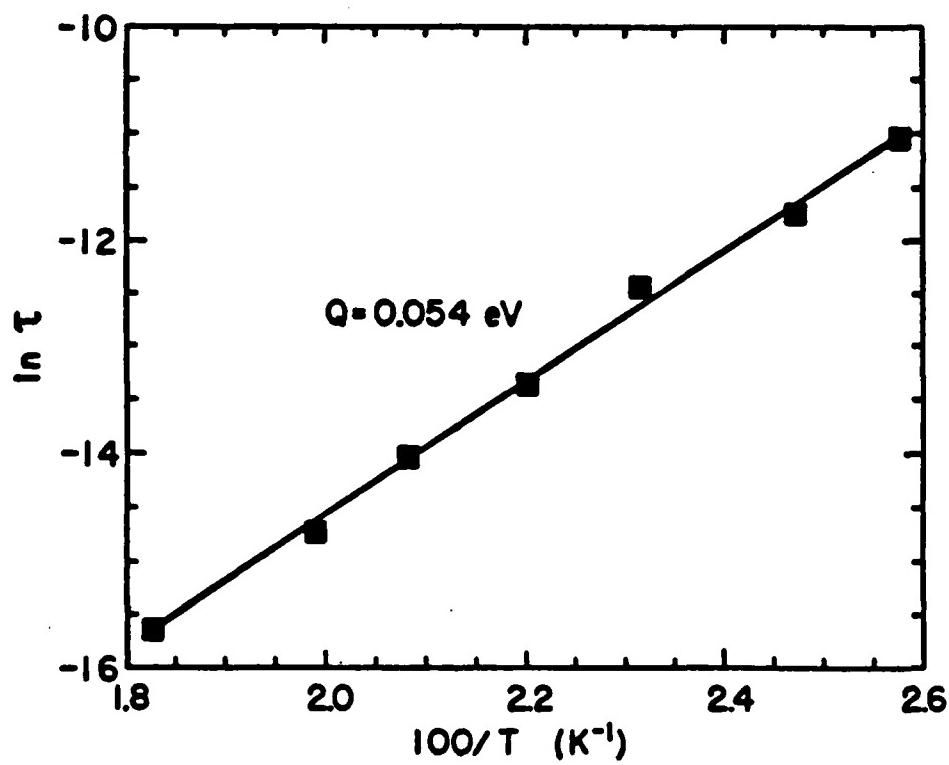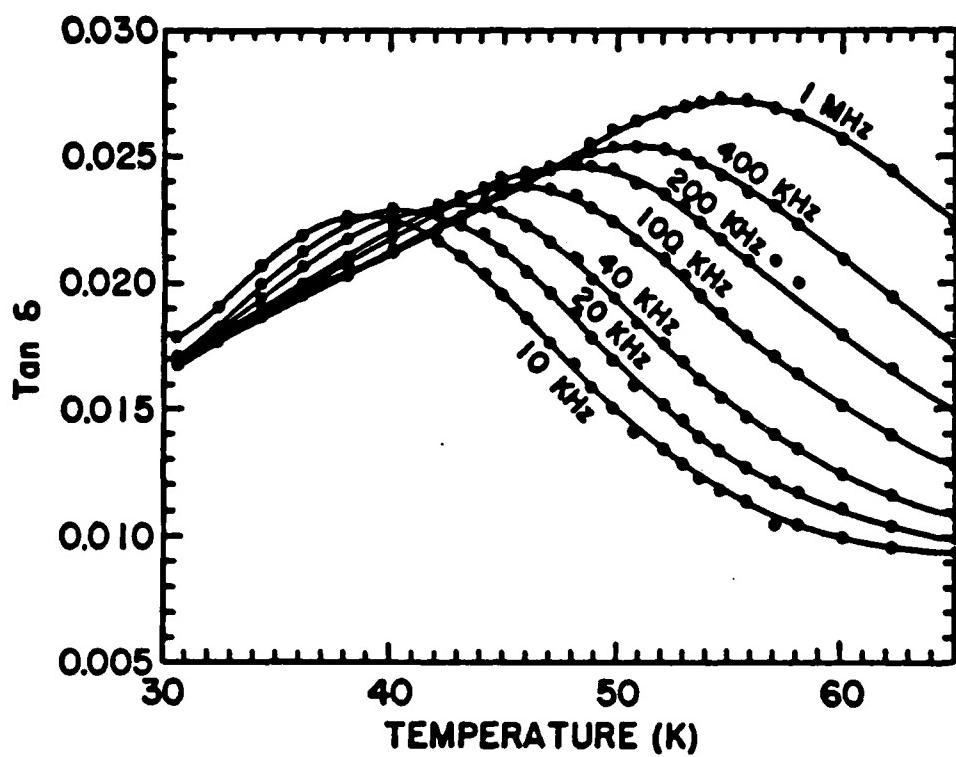
Figure 2
8.5 x 15 cm

Figure 3   8.5x15cm

8.5 x 7cm

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